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ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS IN  
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ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS IN CHEMICALLY  
INERT MICROHETEROGENEOUS SYSTEMS

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Ecole Polytechnique Fédérale de Lausanne

DAJA45-85-C-0026

1st Periodic Report

July 1985 - August 1985

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The reduced solubility of organic materials in practically perfluorinated microemulsions <sup>1)</sup> led to the preparation of perhydrogenated microemulsions containing the appropriate perhydrogenated oil and cosurfactant, but in which the surfactant has been chosen in order to match the critical micellar concentration of the previously perfluorinated carboxylic acid. The pseudo-ternary phase diagram of those perhydrogenated microemulsions shows larger domains of oil/water and water/oil microemulsions; these areas remain, however, at the same range of water, oil and surfactant/cosurfactant percentages as found in the case of the practically perfluorinated microemulsions.

We are interested to test if a high probability of thermodynamically stable mixtures of perfluorinated and perhydrogenated microemulsions can be prepared within those areas. This work would directly lead to a useful method to produce mixed perfluorinated/perhydrogenated microemulsions.

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A glove box for experiments under exclusion of oxygen (argon atmosphere) has been installed; remaining oxygen concentration being traced by an appropriate electrode system. For conductivity measurements in frequently changing media, a flow cell has been mounted in a glass/Teflon lined cycle. The new installation permits conductivity measurements along chosen lines of a pseudo-ternary phase diagram.

Oxidation reactions are performed as planned with alkaline solutions of H<sub>2</sub>O<sub>2</sub>, a frequently used method for cotton and paper pulp bleaching. Despite the industrial use of this reaction, its mechanism has never been reported. First kinetic measurements in homogeneous solution have been made in order to test a specially designed apparatus for oxygen measurements as well as to investigate on intermediates. The results indicate that OH-radicals do not participate decisively in the oxidation

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reaction of secondary alcohols, that  $H_2O_2$  is not consumed in accord with a direct reaction between  $O_2H^-$  and the organic substrate and that most probably  $O_2^-$  is an intermediate in the oxidative sequence.

Experiments with specific trapping agents as well as in micro-emulsions will follow.

All experiments have been made so far under the supervision of Dr. Esther Oliveros. New equipment has been built according to designs made by the principal investigator.

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 1) E. Oliveros, M.-T. Maurette, A.M. Braun, Helv. 66, 1183 (1983)  
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Financial statement

As of August 31, SFR 7668.-- or US\$ 3378.-- have been paid in salaries leaving an amount of unused funds of US\$ 25747.--  
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Lausanne, August 28, 1985

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 André M. Braun

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